

REMARKS

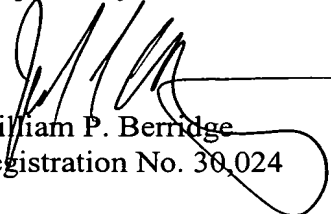
Claims 1-16 are pending in this application.

By this Preliminary Amendment, the specification is amended (by way of submission of a substitute specification) to add section headings and paragraph numbering, and minor grammatical changes are made throughout the specification and Abstract. In addition, claims 1-16 are amended to conform to accepted U.S. claim format, for example, by (1) eliminating multiple dependent claims, (2) revising "characterised in that" to "wherein", (3) revising "use" claim 12, and (4) correcting antecedent basis issues.

In view of the foregoing, it is respectfully submitted that this application is in condition for allowance. An early and favorable action on the merits is earnestly solicited.

Should the Examiner believe that anything further would be desirable in order to place this application in even better condition for allowance, the Examiner is invited to contact the undersigned at the telephone number set forth below.

Respectfully submitted,



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Attachments:

Marked-up Copy of Specification
Substitute Specification

Date: October 1, 2004

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COMPOSITE MATERIAL, METHOD OF PRODUCTION, AND USES THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application is a U.S. national stage application of International Application No. PCT/EP03/03234 filed on March 28, 2003.

BACKGROUND OF THE INVENTION1. Field of Invention

[0002] The invention relates to a composite material, a method for its production, and its uses.

2. Description of Related Art

[0003] Reinforcing fibers and their use, along with a composite resin, for production of composite materials are known. US-U.S. Patent No. 5,641,572 describes reinforcing fibers made from short carbon fibers that contain, for example, polyphenylene sulfide (PPS) as a sizing agent. US-U.S. Patent No. 5,641,572 teaches that the proportion of sizing agent relative to the total weight of short carbon fibers must be at least 0.01 per cent by weight because for a proportion of less than 0.01 wt.% the protective effect is unsatisfactory. US-U.S. Patent No. 5,641,572 also teaches of the carbonization of the sized short carbon fibers in an inert gas at 400 to 1500°C. Following this procedure, the short carbon fibers contain only the products of carbonization of the sizing agent. Finally, US-U.S. Patent No. 5,641,572 discloses the production of a reinforcing material made from the carbonized short carbon fibers and a thermoplastic resin. US-U.S. Patent No. 5,641,572 gives no indication of how the apparent interlaminar shear strength (ILSS) and bending strength of composite materials containing reinforcing fibers can be improved. It is precisely on these properties, however, that increasingly exacting demands are being placed.

SUMMARY OF THE INVENTION

[0004] The object of the present invention is therefore to increase the apparent interlaminar shear strength and the bending strength of composite materials containing reinforcing fibers.

[0005] ~~This object is~~ These and other objects are achieved by a composite material containing a reinforcing resin and reinforcing fibers, the reinforcing fibers having a coating containing polyphenylene sulfide, characterized in that the proportion of polyphenylene sulfide relative to the uncoated reinforcing fibers is 0.001 to < 0.01 wt.%.

[0006] If reinforcing fibers that have been coated in this way are processed by methods that are known ~~per se~~ into a composite material, it is found that the apparent interlaminar shear strength and the bending strength are higher than when reinforcing fibers are used that have not been coated according to the invention. This result is surprising because it could not have been foreseen that such small quantities of PPS would have any effect at all on the composite-material properties, much less that such small proportions by weight of PPS would improve the apparent interlaminar shear strength and the bending strength. Even more surprising is the finding that the apparent interlaminar shear strength and the bending strength of the composite materials of the invention show a maximum in the range of 0.001 to < 0.01 wt.% of PPS relative to the reinforcing fibers. Composite materials of the invention that contain PPS-coated carbon reinforcing fibers and have been processed into a composite material with a polyetheretherketone, for example, show this maximum for a PPS-content, relative to the carbon fibers, of about 0.006% by weight.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0007] In a preferred embodiment of the composite material of the present invention, the proportion of polyphenylene sulfide relative to the uncoated reinforcing fibers is 0.002 to 0.009 wt.%.

[0008] In a ~~further~~another preferred embodiment of the composite material of the invention, the coating ~~consists of~~comprises polyphenylene sulfide and a thermoplastic or duroplastic material, the thermoplastic preferably being a polyetherimide, polyetherketone, polyetheretherketone, polyethersulfone, polyetherethersulfone or polysulfone, and the duroplastic preferably ~~being~~is an epoxy resin.

[0009] The reinforcing resins used in the composite material of the invention are preferably thermoplastics such as polyetherimide, polyetherketone, polyetheretherketone, polyethersulfone, polyetherethersulfone or polysulfone, or a mixture of these thermoplastics.

[0010] The reinforcing fibers for the composite material of the invention can ~~in principle~~ be any fibers of natural or synthetic origin that possess the properties required of reinforcing fibers, the required properties being particularly well developed when the reinforcing fibers are carbon fibers of pitch, polyacrylonitrile or rayon precursors, or aramid, glass, ceramic, boron, synthetic or natural fibers, or ~~combinations~~any combination of these fibers. Polyester fibers are especially preferred as synthetic fibers. Flax, ~~and flax~~ or sisal fibers are preferred as natural fibers.

[0011] A carbon reinforcing fiber especially preferred for the composite material of the invention is available under the name of Tenax HTS® from Tenax Fibers GmbH, Wuppertal, Germany. In the composite material of the ~~invention-invention,~~ the fibers may be present as short-cut fibers or as filament yarn that can ~~consist of~~comprise several thousand filaments, and preferably ~~of~~ between 3,000 and ~~24,000,24,000~~ filaments. The fibers in the composite material of the invention can also be present in the form of a textile fabric such as a woven, nonwoven, knitted or crocheted fabric, or as a ~~uni-~~unidirectional or multidirectional scrim.

[0012] ~~The object~~Objects of the invention ~~is~~are further achieved by a method for production of a composite material comprising the steps

- a) ~~provision of~~providing reinforcing fibers that have been pretreated if required,
- b) ~~application of~~applying a coating containing polyphenylene sulfide on the reinforcing fibers of step a), such that the coating contains 0.001 to < 0.01% wt.% of polyphenylene sulfide relative to the reinforcing fibers, resulting in the production of coated reinforcing fibers, and
- c) ~~processing of~~ the coated reinforcing fibers of step b) into a composite material, using a reinforcing resin.

[0013] In step a), any method of providing the reinforcing fibers is suitable that makes the entire surface of the fibers accessible for the coating to be applied in step b). For example, the freshly spun and dried reinforcing fibers can be fed directly into the production method, either individually or as a yarn sheet, before winding up. Alternatively, the reinforcing fibers can be provided as filament yarn ~~consisting of~~comprising several thousand filaments, preferably ~~of~~ about 3,000 to 24,000 filaments.

[0014] The reinforcing fibers for step a) of ~~the one~~ method of the invention can ~~in principle~~ be any fibers of natural or synthetic origin that possess the properties required of reinforcing fibers,~~the~~ The required properties are ~~being~~ particularly well developed when the reinforcing fibers are carbon fibers of pitch, polyacrylonitrile or rayon precursors, or aramid, glass, ceramic, boron, synthetic or natural fibers, or combinations of these fibers. Polyester fibers are especially preferred as synthetic fibers,~~and flax.~~ Flax or sisal fibers are preferred as natural fibers. Carbon fibers obtainable under the name Tenax HTS® from the firm of Tenax Fibers GmbH, Wuppertal, Germany, are especially preferred as the carbon reinforcing fibers in step a) of the method of the invention.

[0015] The reinforcement fibers provided in step a) of the method of the invention are pretreated if necessary for adequate wetting of the reinforcing fibers with the coating to be applied in step b) and for adhesion of the coating to the reinforcing fibers. Pretreatment of the reinforcing fibers can also improve adhesion of the coated fibers to the reinforcement resin used in step c), if the reinforcing fibers in step b) have not been provided with the coating ~~of the invention~~ over their entire surface. If required, the method used for pretreatment can be an impregnation method, wherein the reinforcing fibers are immersed in hydrophobic or hydrophilic liquid media and dried. Pretreatment methods may also be used in which reactive functional groups are introduced on the surface of the fiber as in electrochemical oxidation, which provides the surface of the reinforcing fibers with, for example, hydroxyl and carboxyl groups.

[0016] For the application in step b) ~~of the method of the invention~~, any method is ~~in principle~~ suitable that is capable of applying ~~on-onto~~ a reinforcing fiber between 0.001 ~~to~~ and < 0.01 wt.% of polyphenylene sulfide relative to the weight of the reinforcing fibers.

[0017] For example, the reinforcing fibers can be conducted in step b) through a PPS melt, having optionally been previously conducted through a melt of a thermoplastic such as polyetherimide. It is also possible to prepare a melt of PPS and a thermoplastic such as polyetherimide, and to conduct the reinforcing fibers through the melt containing both polymers.

[0018] Alternatively, PPS powder can be introduced into a plasma, whereby the PPS particles are accelerated in the direction of the reinforcing fibers, ~~and melt~~. On encountering the reinforcing fibers, the PPS particles solidify and form the required layer on the reinforcing fibers. This plasma spray coating with PPS can be preceded by plasma spray coating with a thermoplastic such as polyetherimide. It is also possible to use PPS and a thermoplastic such as polyetherimide simultaneously in the plasma spray coating.

[0019] Furthermore, PPS application can be integrated into the production process for the reinforcing fibers before wind-up, in which case the known devices for application of finishing agents can be used. A thermoplastic such as polyetherimide can optionally be applied before PPS application. Alternatively, a sizing agent can be prepared from PPS and a thermoplastic such as polyetherimide, and this sizing agent can then be applied to the reinforcing fibers.

[0020] In a ~~preferred~~ another embodiment of the method of the invention, the PPS ~~PPS~~, in the form of ~~crystallites~~ crystallites, is applied on the reinforcing fibers in, for

example, a step b) ~~in which~~ wherein the reinforcing fibers from step a) are conducted through a bath containing a suspension of PPS, ~~dried, dried~~ and wound up. There are no special requirements on the temperature of the bath, provided that at the chosen ~~temperature~~ temperature, the finest possible crystallites of PPS are desirably present in the suspension. In ~~many various~~ embodiments of the ~~method of the invention~~, this is true ~~to an adequate extent~~ even at room temperature, which is therefore the preferred temperature for the bath. ~~It During~~ drying, it is important ~~during drying~~ to prevent decomposition of the coating while also ensuring that moisture adhering to the coated reinforcing fibers is removed. A dryer temperature in the range of 350°C to 400°C is suitable in many cases, the temperature being selected according to the drying time. The reinforcing fibers can optionally first be conducted through a bath containing a solution of a thermoplastic such as polyetherimide, and the fibers that have been wetted with the solution then conducted through a bath containing a suspension of PPS, ~~following which~~ PPS. ~~Then~~ the fibers ~~are would be~~ wound up and dried as described above.

[0021] It is especially preferred that the reinforcing fibers, which may for example be present as filament yarn with 3,000 to 24,000 filaments, be conducted through a ~~bath,~~ the bath. ~~The contents of which the bath comprise~~ consist of a suspension of PPS, a solution of a thermoplastic such as a polyetherimide solution, a solvent, and, if required, an ~~emulsifier,~~ following emulsifier. ~~After the reinforcing fibers are conducted through the bath, which the~~ After the reinforcing fibers are conducted through the bath, ~~which the~~ fibers are dried and wound up as described. The solvent is ~~so~~ chosen so that it dissolves the thermoplastic but not the PPS. A suitable solvent, when the thermoplastic is polyetherimide, is for ~~example example~~ example, 1-methyl-2-pyrrolidone (NMP). An example of a suitable emulsifier is decaethylene glycol oleyl ether. In this case, and in all embodiments of the method of the invention in which a PPS suspension in a bath is used, the suspension is maintained by keeping the bath contents continuously in motion by, for example, pump circulation or stirring. While the reinforcing fibers are conducted through the bath, the yarn tension is preferably 0.3 to 1.5 cN/tex, ~~especially and more~~ preferably 0.5 to 1.0 cN/tex. The speed at which the reinforcing fibers are conducted through the suspension is preferably 60 to 600 m/h, and especially preferably 120 to 480 m/h. The concentration of the PPS suspended in the bath is preferably 0.2 to 5 wt.%, and especially preferably 0.5 to 1.5 wt.% of PPS, relative in each case to the polyetherimide content, the proportion of which in the bath contents ~~lies is,~~ is, for ~~example example~~ example, in the range of 0.5 to 1.0 wt.%, and especially preferably in the range 0.5 to 0.7 wt.%. The parameters cited above are adjusted in such a way that a coating of, for example, 0.5 to 1.0 wt.% and especially preferably of 0.5 to 0.7 wt.% results.

[0022] A suspension with ~~especially~~ finely divided PPS crystallites is obtained when the thermoplastics and PPS are placed in an extruder in the above-mentioned proportion by weight and are melted to obtain a granulate. This granulate is then introduced into the above-mentioned solvent, which may contain an emulsifier if required. The thermoplastic dissolves and the PPS forms a fine-particle suspension. The PPS proportion, ~~according to the invention,~~ in the reinforcing fiber can be adjusted by adjusting the PPS concentration in the bath through which the reinforcing fibers pass at the prescribed speed, such that the coated reinforcing fibers contain 0.001 to < 0.01 wt.% of PPS.

[0023] The proportion by weight of the coating on the reinforcing fibers is determined by Method B in DIN EN ISO 10548. If the coating of the fibers contains a thermoplastic in addition to PPS, the proportion by weight of PPS in the coated reinforcing fibers is calculated from the ratio of the weights of thermoplastic and PPS used for coating.

[0024] In step c) of the method of the invention, the coated reinforcing fibers are processed with a reinforcing resin, preferably a thermoplastic or a mixture of thermoplastics, to give a composite material. ~~Especially suitable~~ Suitable thermoplastics include polyetherimides, polyetherketones, polyetheretherketones, polyethersulfones, polyetherethersulfones or polysulfone, or a mixture of these thermoplastics. The methods by which the reinforcing fibers coated by the method of the invention are processed into composite materials are known ~~per se~~. They include, for example,

- (1) mixing of reinforcing fibers that have been coated by the method of the invention with fibers or a powder or a film of composite resin and subsequent hot pressing,
- (2) impregnation of reinforcing fibers that have been coated by the method of the invention with a melt or solution of composite resin, and
- (3) compounding of reinforcing fibers that have been coated by the method of the invention and cut to short fibers.

[0025] The reinforcing fibers that have been coated by the method of the invention can be further processed to a composite material in the form in which they occur after step b) ~~of the method of the invention~~, e.g., as filament yarn.

[0026] Alternatively, the coated reinforcing fibers resulting from step b) of the method of the invention could first be brought into the form of a textile fabric and processed in this form into a composite material. For example, the coated reinforcing fibers resulting from step b) ~~of the method of the invention~~ could first be processed into a nonwoven fabric or cut into short fibers. The reinforcing fibers coated by the method of the invention could also

first be brought into the form of a woven, braided, knitted or crocheted fabric, or of a ~~uni-~~unidirectional or multidirectional scrim.

[0027] In the production of the composite material in step c), the coated reinforcing fibers ~~coated by the method of the invention~~ show outstanding impregnation behavior on hot pressing with polyetheretherketone in regard to penetration of the polyetheretherketone into the filament yarn as well as wetting of the individual coated filaments. The composite materials of the invention have a fiber proportion of 40 to 70 vol.%, the fiber proportion for laminates of unidirectional prepregs preferably lying in the range of 55 to 65 vol.%, for laminates of fabric prepregs in the range of 45 to 55 vol.%, and for wound or pultruded bodies in the range of 55 to 70 vol.%.

[0028] The apparent interlaminar shear strength of the composite materials of the invention is measured as in DIN EN 2563, and the bending strength (0° in the fiber direction and 90° perpendicular to the fiber direction) as in DIN EN 2562.

[0029] The composite material of the invention and composite material produced by the method of the invention can advantageously be used to produce components for aircraft construction, such as the body and landing flaps; for automobile construction, such as engine parts, pumps and seals; for machine construction and plant construction, such as seals, bearings and tanks; and for production of medical components such as surgical instruments.

[0030] The invention will now be described in more detail with the help of the following examples.

Example 1

[0031] 98 parts by weight of polyetherimide (Ultem® from GE Plastics) and 2 parts by weight of PPS (Fortron® from Ticona) are placed in an extruder and melted, and a granulate is produced. 39 g of the granulate ~~are~~is stirred into 590 g of hot 1-methyl-2-pyrrolidone (NMP) until the polyetherimide has dissolved. The PPS does not dissolve, and forms a suspension. A mixture consisting of 200 g of NMP, 60 g of water and 20 g of the emulsifier decaethylene glycol oleyl ether is added dropwise to the stirred polyetherimide solution and PPS suspension, which has been cooled to 70°C. The resulting mixture is stirred into 600 ml of warm water at 50°C so that an emulsion is formed, which is kept in continuous motion by pump circulation. The obtained solution ~~so obtained~~ is diluted with water until the resulting solution consists of 0.6 wt.% of polyetherimide, 0.006 wt.% of PPS, 0.3 wt.% of decaethylene glycol oleyl ether, 12.2 wt.% of NMP and 86.894 wt.% of water.

[0032] A filament yarn with a linear density of 800 tex and made from carbon fibers, which are available under the name Tenax HTS[®] from Tenax Fibers GmbH and have been pretreated by electrochemical oxidation, are conveyed through the emulsion described above with a yarn tension of 1.0 cN/tex and at a speed of 180 m/h, dried at 350°C and wound up. The proportion of PPS relative to the carbon fibers is 0.006 wt.% (see Table, Example 1).

[0033] The filament yarn is processed into a composite material with polyetheretherketone, available under the name PEEK[®] 151 G from Victrex. The polyetheretherketone is used in the form of a film. This film and the coated Tenax HTS[®] fibers are arranged in alternating layers, which are then laminated together at a pressure of ~~approx.~~approximately 9 bar and a temperature just above 400°C. Following ~~lamination~~lamination, the temperature in the composite material is reduced to room temperature within 24 h.

[0034] The apparent interlaminar shear strength is 143 MPa, the bending strength (0°) is 3380.4 MPa, and the bending strength (90°) is 187 MPa (see Table, Example 1).

Example 2

[0035] Example 1 is repeated with the difference that the emulsion consists of 0.597 wt.% of polyetherimide, 0.009 wt.% of PPS, 0.3 wt.% of decaethylene glycol oleyl ether, 12.2 wt.% of NMP and 86.894 wt.% of water. The proportion of PPS relative to the carbon fibers is 0.009 wt.% (see Table, Example 2).

[0036] The interlaminar shear strength is 125 MPa, the bending strength (0°) is 2972.1 MPa, and the bending strength (90°) is 153 MPa (see Table, Example 2).

Comparative Example

[0037] Example 1 is repeated with the difference that the emulsion contains no PPS and consists of 0.606 wt.% of polyetherimide, 0.3 wt.% of decaethylene glycol oleyl ether, 12.2 wt.% of NMP and 86.894 wt.% of water (see Table, Comparative 3-Example V).

[0038] The apparent interlaminar shear strength is 121 MPa, the bending strength (0°) is 2473.3 MPa, and the bending strength (90°) is 152 MPa (see Table, Comparative 3-Example V).

[0039] The following table shows the percentage by weight of PPS relative to the carbon fibers (wt.% PPS), the interlaminar shear strength (ILSS), the bending strength (0°) as BS (0°) and the bending strength (90°) as BS (90°).

Example	wt.% PPS	ILSS MPa	BS (0°) MPa	BS (90°) MPa
1	0.006	143	3380.4	187
2	0.009	125	2972.1	153
<u>✓Comparative 3</u>	0.000	121	2473.3	152

[0040] It is seen from the table that the ILSS and the BS at 0° and 90° are maximum for a PPS proportion of 0.006 wt.% relative to the carbon fibers.